Glycerolysis for Lowering Free FattyAcid of Waste Cooking Oil

[1*]M. Dani Supardan, [1]Adisalamun, [2]Yanti Meldasari, [2]Yulia Annisa, [3]Mahlinda

[1]Department of Chemical Engineering, Syiah Kuala University,Darussalam, Banda Aceh 23111, Indonesia
[2]Department of Agriculture Product Technology, Syiah Kuala University,Darussalam, Banda Aceh 23111, Indonesia
[3]Balai Riset dan Standardisasi Industri Banda Aceh, Indonesia
*Coorresponding Author: m.dani.supardan@che.unsyiah.ac.id

Abstract

Glycerolysis can be a useful alternative for lowering free fatty acid content present in the sustainable feedstock of waste cooking oil. In the present work, the effect of reaction parameters such as molar ratio of oil to glycerol (1:1, 1:2 and 1:3), catalyst NaOH concentration (0.875, 1.3 and 1.75 %-w of oil) and mass ratio of oil to co-solvent hexane (2:1, 4:1, 8:1) have been investigated. The reaction parameters have a remarkable effect on the free fatty acid (in term of acid value) of waste cooking oil. The final acid value decreased with an increased in molar ratio of oil to glycerol from 1:1 to 1:2. A significant reduction in acid value was not observed with a further increase in molar ratio of oil to glycerol. It has been observed that the optimum catalyst concentration of 1.3% can be reduced acid value from 12.2 to 1 mg KOH/g oil in 20 min. The addition of hexane as co-solvent affected the reaction rate due to immiscibility of the oil and glycerol phases. However, a suitable amount of co-solvent must be added to achieve an optimum of acid value reduction.

Key words: acid value, free fatty acid, glycerolysis, waste cooking oil

Introduction

The glycerolysis process has the capability of converting the free fatty acid (FFA) back to their respective glyceride molecule. In glycerolysis, the glycerol reacts with the FFA to form monoglycerides, diglycerides and triglycerides (Anderson, 1962). It produces a low FFA feedstock that can be further processed using homogeneous base transesterification. The advantage of this approach is that no alcohol is needed during the pre-treatment process. The process has the potential of utilizing glycerol, a by-product from transesterification thereby lowering the cost of process. However, the drawbacks of this method are its high temperature requirement, relatively slow reaction rate and being limited by equilibrium, having two liquid phases, where the solubility of glycerin is rather limited in triglycerides (Felizardo et al., 2011). This has limited the application of glycerolysis in pre-treatment of FFA for production of more valuable product. Despite of its potentiality in lowering high FFA, glycerolysis process has been commonly used to produce monoglycerides and diglycerides, which are widely used as surfactants and emulsifiers in food, cosmetic, and pharmaceutical products.

The glycerolysis process can be carried out via enzymatic, alkaline and acid catalyzed reactions (Sonntag, 1982). Most of the existing literature on glycerolysis utilizes high temperature and low pressure in the process. The literature also shows that the important variables that affect the glycerolysis reaction are reaction temperature, type and amount of

catalyst, molar ratio of glycerol to oil, the mixing intensity and the reaction time (Noureddini et al., 2004; Felizardo et al., 2011; Gole and Gogate, 2014; Cai et al., 2015). Recently, Kombe et al. (2013) reported the application of low temperature glycerolysis for pre-treatment of oil with high FFA. Based on optimisation study, the highest glycerolysis efficiency of 98.67% were found to be temperature of 65°C, reaction time of 73 minutes and glycerol to oil mass ratio of 2.24.

In this study, the low temperature base catalyzed glycerolysis has been applied for lowering of high FFA in waste cooking oil via homogeneous base catalyst. The effect of reaction parameters such as molar ratio of oil to glycerol, catalyst NaOH concentration and mass ratio of oil to co-solvent hexane have been investigated.

Materials and methods

Materials

Waste cooking oil was collected from restaurants around Banda Aceh, Indonesia. Prior to the use in the actual experiments, oil was filtered to remove the traces of particles and mud in the oil. The initial acid value of the oil was observed to be 12.2 mg of KOH/g of oil. Glycerol used in the experiments was of technical grade and NaOH (99%) in pellet form were of analytical grade. All the chemicals were used as received from the supplier. Distilled water, freshly prepared in the laboratory, was used for the preparation of solutions of required concentrations.

Glycerolysis

Glycerolysis reaction was carried out in a glass batch reactor equipped with IKA RW20 mechanical digital stirrer. Waste cooking oil was heated and maintained at a given set temperature. A specified portion of NaOH catalyst was dissolved in glycerol before mixing with oil at 600 rpm using IKA RW20 mechanical digital stirrer. Then, the reaction mixture was mixed and heated for the desired duration. The reaction temperature was kept constant at 65 ^{o}C for all the experimental runs. Samples were taken at specific interval of time. The sample was cooled to room temperature before separation and then poured into a separating funnel and allowed to form two layers. The heavier phase glycerol, dissolved catalyst and other minor components from the oil easily separated as a lower layer. The acid value of the upper layer was measured to monitor the progress of the reaction.

Method of analysis

The main objective of glycerolysis is to reduce the free fatty content in oil, which can be monitored in terms of the acid value of oil. The acid–base titration technique was used to determine the acid value of oil. A standard solution of 0.1 M of alcoholic potassium hydroxide was prepared by dissolving KOH in ethanol. A sample of 1 g of oil was dissolved in ethanol and heated for 5–10 min. The known quantity of sample was then titrated against potassium hydroxide using phenolphthalein as an indicator.

Results and Discussion

Effect of molar ratio of oil to glycerol

Glycerolysis of FFA is a reversible reaction (Moquin et al., 2005). The reaction scheme is shown in Fig. 1. From the reaction stoichiometry, it is observed that 1 mol of glycerol is required to complete the reaction. As consequence, glycerol is usually taken in excess amount with an objective of driving the reaction in the forward direction.

To investigate the effect of excess glycerol on the progress of the reaction, various oil to glycerol molar ratios of 1:1, 1:2 and 1:3 have been selected at constant catalyst concentration of 1.75 %-w. The change in acid value with the reaction time at different

molar ratio has been given in Fig. 2. It has been observed that the final acid value of oil decreases with an increase in molar ratio from 1:1 to 1:2 i.e., when a higher molar ratio than stoichiometrically required ratio is used.

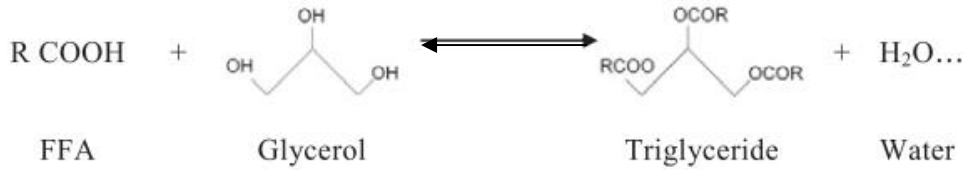

Figure 1. Reaction scheme for glycerolysis of free fatty acid

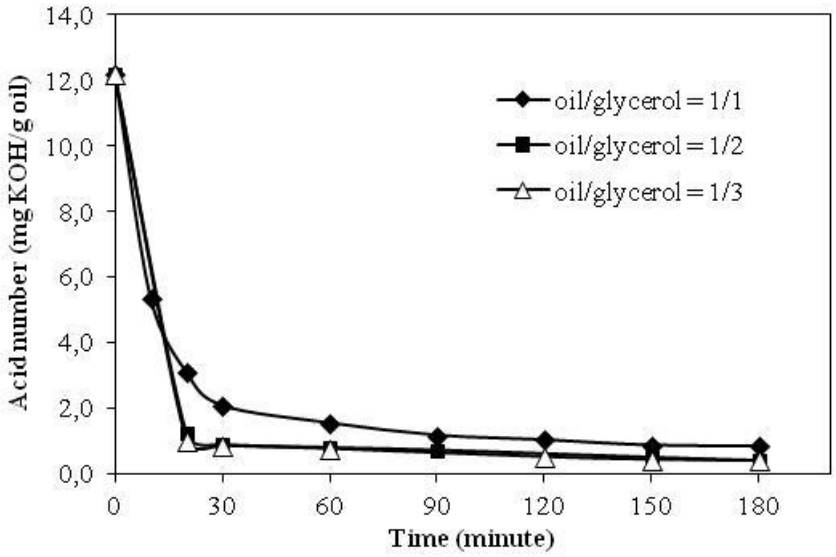

Figure 2. Effect of oil to glycerol molar ratio on reaction progress

It has been observed that a molar ratio of 1:2 and reaction time of 30 min is sufficient to reduce the acid value from 12.2 to 0.7 mg of KOH/g. With a further increase in the molar ratio from 1:2 to 1:3, significant reduction in acid value was not observed. Similar trends have been reported in the literature for different systems. Acid value reduction of acidulated soap-stocks was achieved from 80 to 7.8 mg of KOH/g for 1:4 of oil to glycerol molar ratio and 200 min of reaction time (Felizardo et al, 2011). The acid value was reduced from 12 to 1 mg of KOH/g for a molar ratio of 1:2 and a reaction time of 150 min for the case of animal fat as sustainable feedstock (Gerpen et al., 2004). Meanwhile, Kombe et al. (2013) reported that a glycerolysis efficiency of 99.72% could be obtained in glycerolysis of crude jatropha oil at optimum conditions 73 minutes of raection time, 1:4 of glycerol to oil molar ratio and 65°C of reaction temperature.

Effect of catalyst concentration

Glycerolysis was also studied by changing the catalyst concentration over the loading of 0.875 to 1.75 %-w for molar ratio of oil to glycerol of 1:1. Figure 3 shows the change in the acid value with reaction time at different catalyst concentrations. It has been observed that the trend result was similar in terms of decreased in acid value with increase in the reaction time. The final acid value also decreased with an increase in the catalyst concentration from 0.875 to 1.3 %-w though beyond this optimum catalyst concentration, the reduction in final acid value was significant.

Based on the experiments with varying catalyst concentrations, it can be concluded that the optimum catalyst loading of 1.3 %-w is sufficient for reducing acid value from 12.2 to 1 mg

of KOH/g in 20 min. The role of catalyst is to provide the active surface for enhancing the rate of reaction. An excess amount of catalyst, however, decreased the rate of reaction. Also, an excess amount of catalyst increases the load on the separation steps and hence selecting the optimum catalyst loading is very important. Cai et al. (2015) reported the optimum NaOH catalyst concentration was 0.5% for glycerolysis of WCO with acid value of 124.9 mg KOH/g at 210 °C of reaction temperature and 4 h of reaction time.

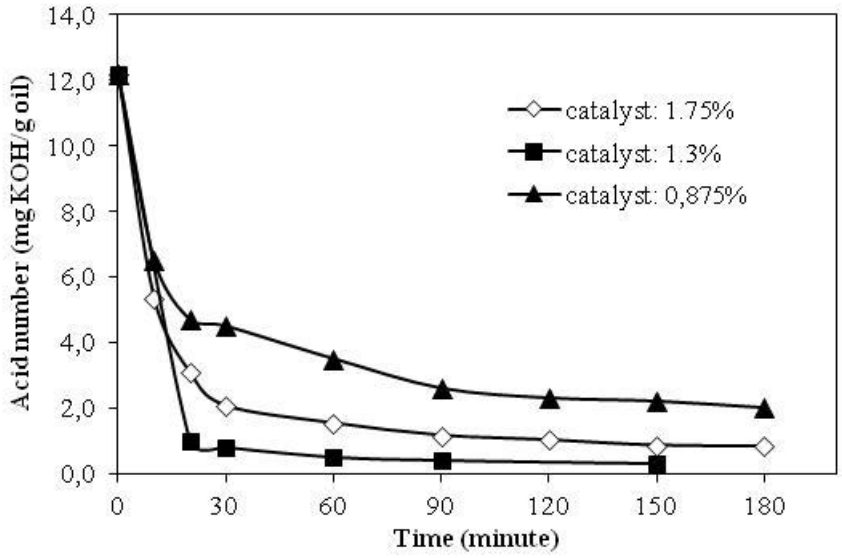

Figure 3. Effect of catalyst concentration on reaction progress

The catalyst requirement is dependent on many factors such as reaction conditions and the properties of feedstock. Selection of optimum catalyst loading is crucial for reducing the raw material cost as well as in deciding the utility requirement for catalyst separation and final product purification.

Effect of co-solvent

In a glycerolysis system, the mass transfer between the two phases of oil and glycerol becomes a significant factor that affects the reaction rate due to immiscibility of the oil and glycerol phases. Co-solvent of hexane could be added to enhance the miscibility of the phases and speed up the reaction rate (Qian et al., 2010; Supardan et al., 2015). The effect of co-solvent of hexane addition on the rate of glycerolysis has been studied by varying the oil to co-solvent weight ratio. The molar ratio of oil to glycerol at 1:1 and catalyst concentration of 0.875 %-w of oil were kept constant for studying the effect of co-solvent addition. The progress of reaction, monitored in terms of the change in the acid value, at different oil to co-solvent weight ratio has been shown in Fig. 4.

It has been observed that acid value generally decreases from an initial value of 12.2 mg KOH/g with an increase in the time of reaction. The final value obtained at the end of time of 180 min was found to be dependent on the oil to co-solvent weight ratio. The final acid value reduced with an increase in the oil to co-solvent weight ratio from 2:1 to 8:1.

As shown in Fig. 4, the final acid values of oil to co-solvent weight ratio of 2:1 and 4:1 are lower compared to the system without cosolvents. Based on the experimental results, it can be concluded that the addition of co-solvent favors the reaction, which can be attributed to better homogeneity of the reaction mixture. However, a suitable amount of hexane must be added to achieve an optimum biodiesel yield. The final acid value further increased at oil to co-solvent weight ratio of 8:1. It might be due to a dilution effect of the excess of hexane. Excessive addition of hexane into the reaction system also could increase the operating

cost. At oil to co-solvent weight ratio of 2:1, the reaction rate is maximum and sufficient to lower the acid value below the desired value required for further processing and hence it can be considered as the optimum oil to co-solvent weight ratio.

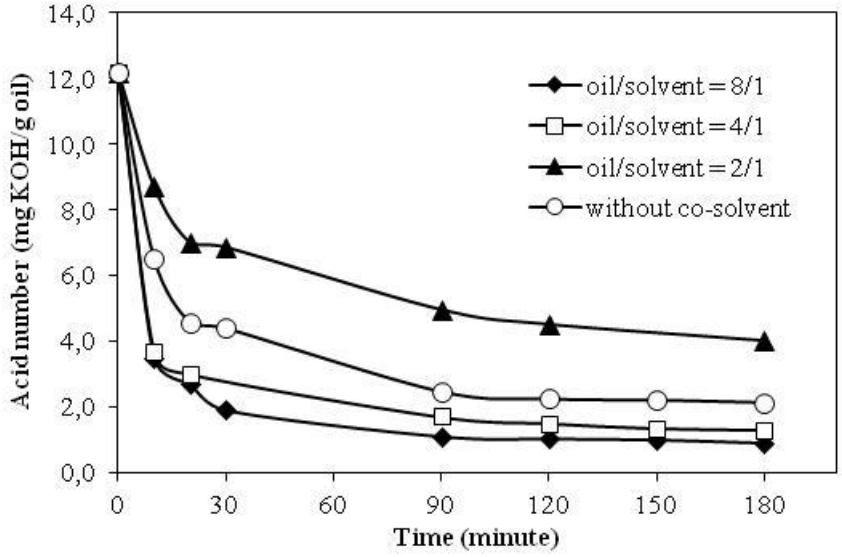

Figure 4. Effect of oil to co-solvent weight ratio on reaction progress

Conclusion

It has been observed that the reaction parameters such as molar ratio of oil to glycerol, catalyst concentration and mass ratio of oil to co-solvent hexane have a remarkable effect on the acid value of waste cooking oil. Generally, acid value decreased with an increased in the time of reaction Experimental result showed that the final acid value decreased with an increased in molar ratio of oil to glycerol from 1:1 to 1:2, however, a further increase in molar ratio of oil to glycerol from 1:2 to 1:3 was not provided a significant reduction in final acid value of oil. The acid value was reduced from 12.2 to 0.7 in 10 min by using catalyst concentration of 1.3%. Meanwhile, a suitable amount of hexane should be added to achieve an optimum of acid value reduction. The lowest final acid value was achieved at a mass ratio of oil to hexane of 8:1. The results showed that glycerolysis is a promising pretreatment for lowering free fatty acid of waste cooking oil. The glycerolysis led to the production of an intermediate material with a low content of free fatty acid that can be used for further processing such as transesterification reaction for the production of biodiesel.

Acknowledgement

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